

*Chapter 12***Electronic and chemical properties of Pd in bimetallic systems: How much do we know about heteronuclear metal-metal bonding?****José A. Rodriguez**Chemistry Department, Brookhaven National Laboratory, Upton, New York
11973, USA**1. INTRODUCTION**

In many industrial applications, bimetallic systems are superior over their single metal-metal counterparts in terms of catalytic activity and/or selectivity [1-4]. For a long time it has been known that a bimetallic surface can exhibit chemical and catalytic properties that are very different from those of the surfaces of the individual metals. Systematic research on alloy catalysts started in the late 1940s [5-7] with *the purpose of establishing links between the electronic and catalytic properties of a surface*. A knowledge necessary for a scientific design of catalysts. However, due to the lack of adequate techniques for the preparation and characterization of the surface alloys, no real progress was made at an experimental level. In the 1960s and 1970s the development of bimetallic catalysts for hydrocarbon reforming in the petrochemical industry increased the need for a fundamental understanding of the behaviour of bimetallic surfaces, and renewed the interest in catalysis by alloys [2,3,8,9]. This effort provided the basis for the concepts of "ensemble" and "ligand" effects [3,9], which are frequently used to rationalize the superior performance of bimetallic catalysts. "Ensemble" effects are defined in terms of the number of surface atoms needed for a catalytic process to occur. Changes in catalyst composition modify the ensembles of available active sites. "Ligand" effects refer to those modifications in catalytic activity or selectivity that are the product of electronic interactions between the components of the bimetallic system. Over the years, it has become clear that it is difficult to find pure "ensemble" or "electronic" effects [10]. In the last two decades, the development of new experimental techniques [11,12] and reliable theoretical methods [13,14] have

The magnitude of the of the binding-energy shift in the Pd 4d band depends on the position of the metal substrate in the Periodic Table. Figure 3 shows the electronic perturbations observed for Pd in surface alloys (PdTi [46] and PdAl [47,48]) and Pd monolayers supported on several metals (Ta(110) [25], Mo(110) [15,45], W(110) [26], Re(0001) [27], Ru(0001) [27] and Al(111) [49]). The experimental results are ordered according to the group in the Periodic Table of the metal bonded to Pd. One finds that the electronic perturbations for the bonding of Pd to s,p metals like Al [47-49] or Zn [35,50] are as large as those seen for Pd bonded to early-transition metals, and much bigger than those found when Pd is bonded to late-transition metals. In general, the magnitude of the shift in the Pd valence levels increases when the fraction of empty states in the valence band of the metal substrate rises [23,48]. This phenomenon could result from a simple hybridisation of the admetal and substrate valence bands [14,25]. In addition, a substrate induced Pd(4d)→Pd(5s,5p) rehybridization could contribute to it [23,51,52]. It is interesting that the systems with the largest shifts reported for the centroid of the Pd 4d band (Pd/Al, Pd/Zn, Pd/Ti) also undergo alloy formation [46-50]. Indeed, results to be shown bellow show a correlation between the strength of the bimetallic bond and the size of the electronic perturbations in Pd.

The core levels of Pd are also very sensitive to the formation of bimetallic bonds. Figure 4 shows Pd 3d XPS spectra for different coverages of Pd on

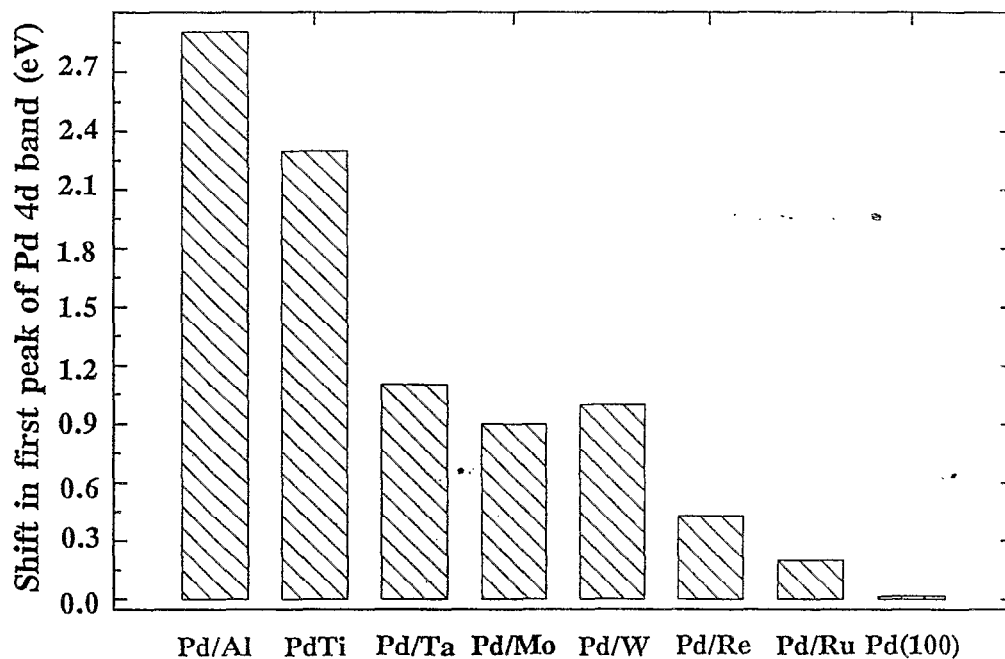


Fig. 3 Effects of bimetallic bonding on the properties of Pd: Shift in the first peak of the Pd 4d band, the one closer to the Fermi level, as a function of metal substrate. Reprinted from ref. [15].

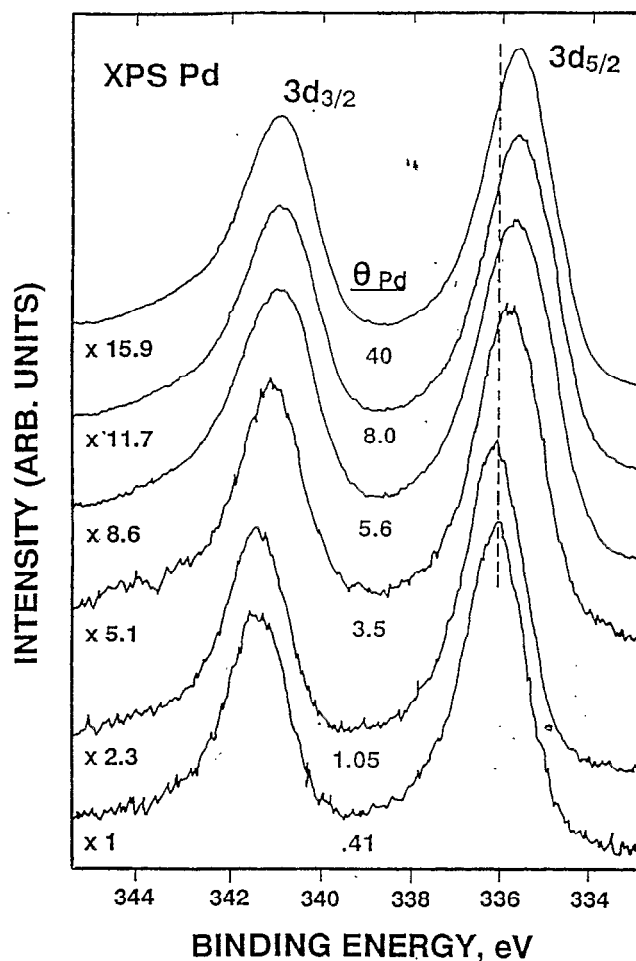


Fig. 4 Palladium 3d core-level spectra for the Pd/W(110) system. Reprinted from ref. [53].

W(110) [53]. There is no observable change with coverage in the separation of the Pd 3d core levels. In the top panel of Figure 5, one can observe that the supported Pd monolayer has a Pd $3d_{5/2}$ binding energy *substantially larger* than that seen for Pd multilayers. Photoemission studies indicate that the Pd $3d_{5/2}$ binding energy of the surface atoms of Pd(100) is ~ 0.4 eV *smaller* than that of bulk Pd [54]. When this is taken into consideration [53], one finds that palladium atoms bonded to W(110) have 3d core levels shifted ~ 0.85 eV toward higher binding energy with respect to those of the surface atoms of pure palladium. The perturbations induced by W on the Pd core levels affect not only the first layer in direct contact with the substrate but also subsequent layers (see Fig 5) [53]. This phenomenon has been also observed on Re(0001) [27] and Mo(110) [44].

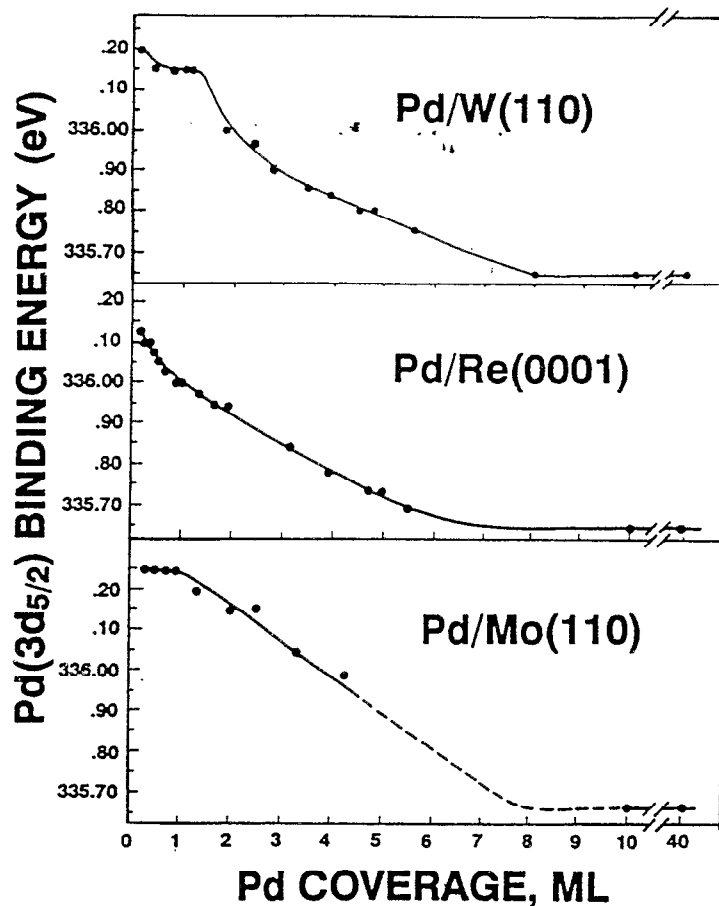


Fig. 5 Palladium 3d_{5/2} core-level positions for Pd/W(110), top, Pd/Re(0001), center, and Pd/Mo(110), bottom, as a function of Pd coverage. Reprinted from refs. [27,44].

Figure 6 compares 3d_{5/2} core-level binding-energy shifts for the deposition of Pd in several metal substrates: Al(111) [48], Ti [15,46], Ta(110) [25,27], Mo(110) [15], W(110) [53], Re(0001) [27] and Ru(0001) [27]. In all cases, bimetallic bonding shifts the Pd core levels towards higher binding energy. The electronic perturbations in Pd are larger when the element is bonded to a s,p metal or to a transition metal with a valence band almost empty. The case of Pd/Re(0001) is particularly interesting because the Pd adlayer is pseudomorphic to the Re substrate, with an atomic density and structure that are very similar to those of the surface atoms in Pd(111) [27]. Yet, the admetal atoms in Pd/Re(0001) are electronically and chemically perturbed due to the effects of bimetallic bonding [27]. The trends in Figures 3 and 6 are identical. In fact, one can say that the shifts in the Pd core levels track shifts in the centroid of the Pd

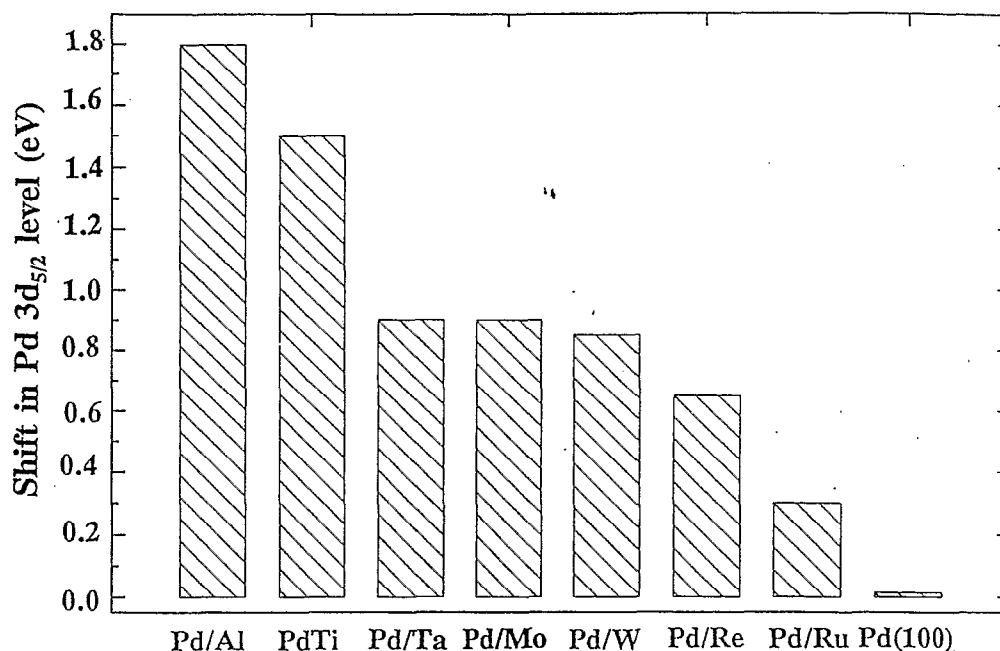


Fig. 6 Effects of bimetallic bonding on the properties of Pd: Shift in the Pd 3d_{5/2} core level as a function of metal substrate. Reprinted from ref. [15].

4d band [15,17]. Although the magnitude of the shifts in the core and valence levels is different in many cases. The type of perturbations seen for Pd in the bimetallic surfaces are similar in many aspects to those found in bulk alloys, where heteronuclear metal-metal bonding induces an increase in the binding energy of the core levels and valence band of Pd [56-59]. Results of x-ray absorption spectroscopy indicate that this phenomenon is accompanied by a reduction in the d electron population of Pd [51,52].

Core-level shifts have been detected in many bimetallic surfaces [15]. Other admetals also exhibit well defined trends as seen for Pd [15]. For example, Figure 7 displays core-level shifts measured after depositing a monolayer of Pt or Ni on a series of metal substrates [23]. Two clear trends can be observed in these experimental data. First, the magnitude of the core-level shift for an admetal increases when the fraction of empty states in the valence band of the metal substrate rises: Ru < Ti < Al. And second, the larger the occupancy of the admetal d band, the bigger the core level shift in the admetal: Ni < Pt < Pd [23]. The largest electronic perturbations are found in systems that combine an admetal with an electron-rich d band and a substrate with an electron-poor valence band.

A priori, it is not clear what causes the core level shifts in Figures 4-7 and, in particular, if the shifts come from initial state effects [60,61]. In principle,

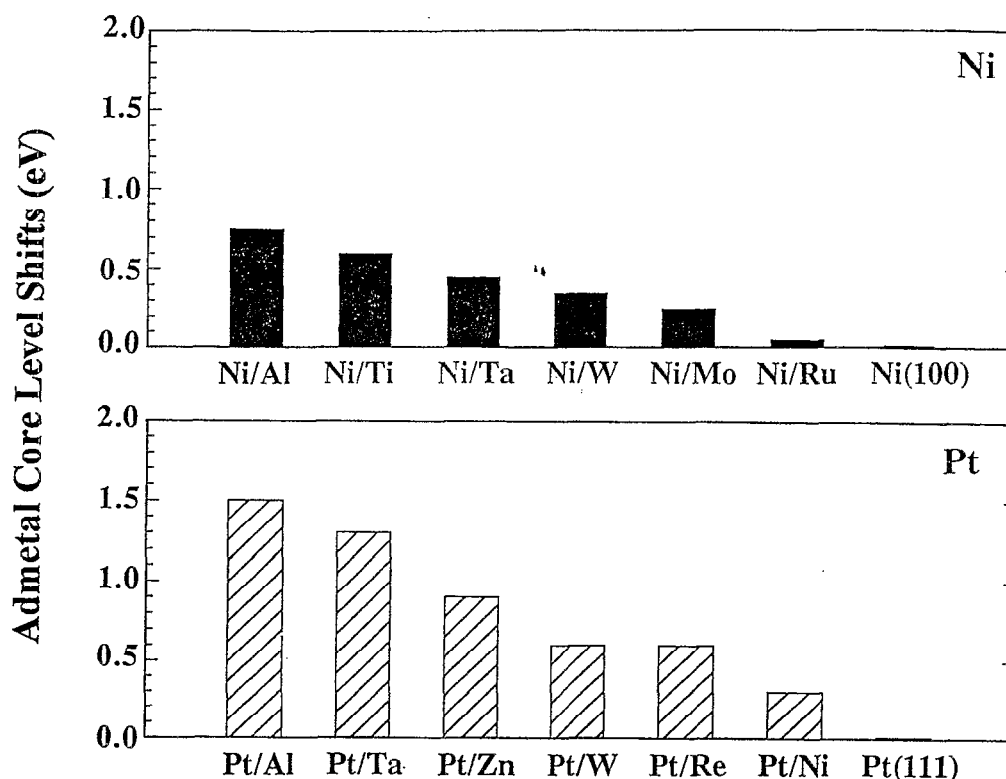


Fig. 7 Core-level shifts for supported monolayers of Ni and Pt as a function of metal substrate. Reprinted from ref. [23].

binding-energy shifts in core-level photoemission can be a consequence of initial state effects (i.e. real variations in the position of the core level produced by charge transfer, orbital rehybridization, volume perturbations, changes in chemical environment, etc) and/or final state effects (i.e. “artifacts” produced by changes in the screening of the core hole) [60-62]. The good agreement between the trends in Figures 3 and 6 suggests that the core level shifts, at least in part, originate from initial state effects. Direct support for this idea is also provided by the experimental data presented in the next two sections. And the theoretical results discussed towards the end of this chapter confirm that, indeed, the core level shifts reflect initial state effects.

3. THERMAL DESORPTION STUDIES

In bimetallic systems like Pd/Al, Pd/Ti and Pd/Zn the bonding interactions between the metals are so strong that intermixing and formation of bulk alloys take place [35,46-50]. Alloy formation does not occur in many other bimetallic systems (Pd/Ta [25], Pd/W [26,53], Pd/Re [27], Pd/Ru [27], Pd/Rh [27]) and one can examine the strength of the corresponding bimetallic bonds using

thermal desorption mass spectroscopy [22]. Typical results are shown in Figure 8. After depositing Pd on Rh(111) and taken TDS spectra, two desorption states of palladium are seen [32]. The high temperature peak (at ~ 1390 K) corresponds to desorption of the first palladium monolayer (i.e. cleavage of Pd-Rh bonds). The low temperature peak (onset at ~ 1200 K) is due to multilayer Pd desorption [63-67], and its intensity grew continuously with increasing palladium coverage [32]. These results show a clear difference (~ 6 kcal/mol) in the strength of the Pd-Rh and Pd-Pd bonds. Even higher desorption temperatures have been reported for Pd atoms bonded to Ta(110) [63,64], Mo(110) [65], W(110) [66,67], Re(0001) [27] and Ru(0001) [27].

Figure 9 compares desorption temperatures and core-level binding energy shifts observed for a monolayer of palladium on Ta(110) [27,63,64], W(110)

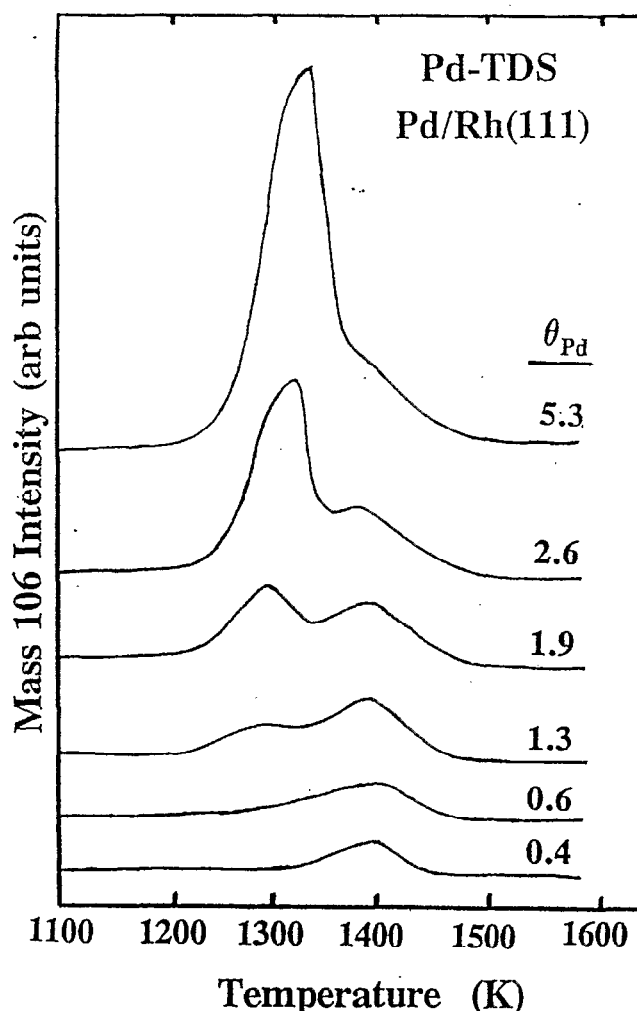


Fig. 8 Thermal desorption spectra ($m/e = 106$) for Pd films on Rh(111). Pd was vapor deposited at a sample temperature of ~ 300 K. Heating rate = 7 K/s. Reprinted from ref. [32].

[53,66,67], Mo(110) [15,65], Re(0001) [27], Ru(0001) [27] and Rh(111) [32]. When going from a rhodium to a tantalum substrate, there is an increase of ~ 150 K in the palladium desorption temperature, which indicates an enhancement of 10-12 kcal/mol in the strength of the Pd-substrate bond. At the same time, the Pd $3d_{5/2}$ core-level shift increases by more than a factor of four. *The stronger the bimetallic bond, the larger the electronic perturbations in the Pd atoms.* The strongest metal-metal bonds are seen in systems that combine a metal with an electron-rich d band (Pd) and a substrate with an electron-poor d band (Ta, W, Mo).

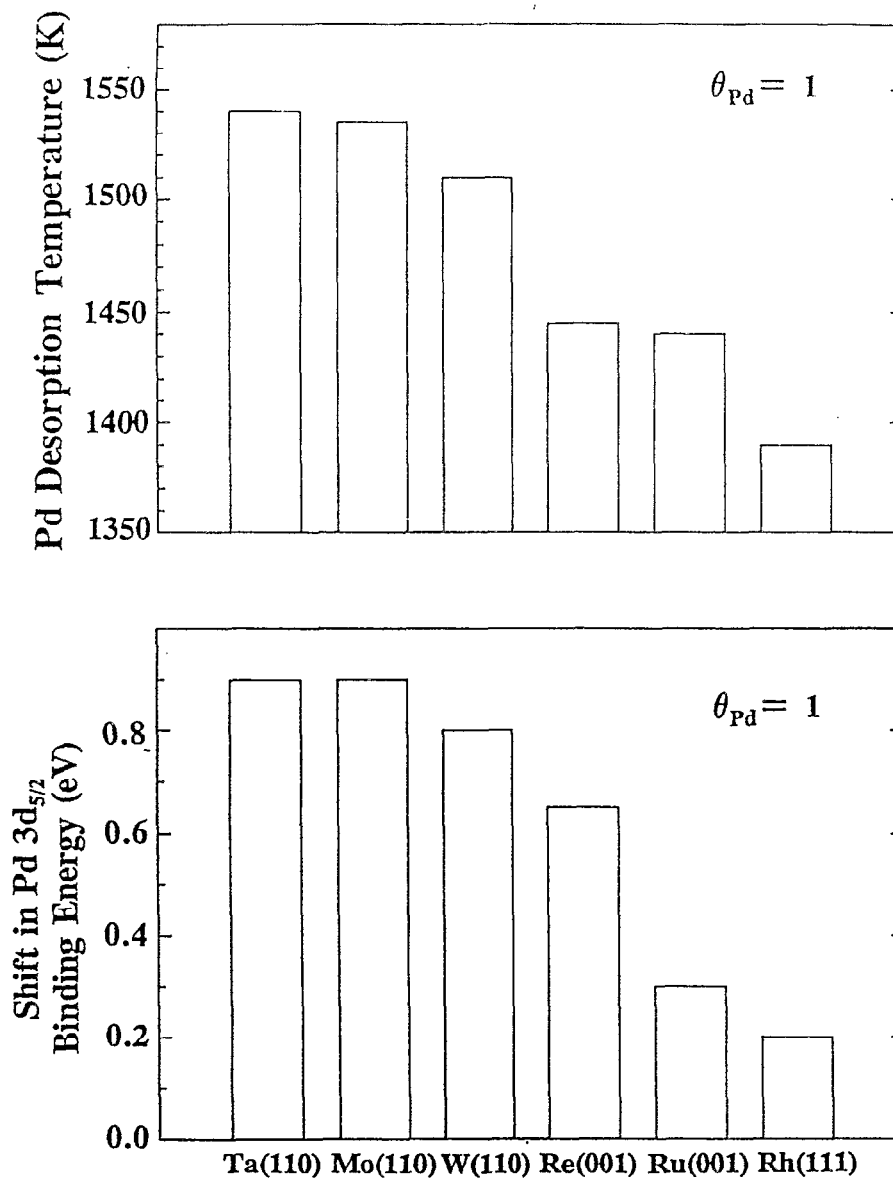


Fig. 9 Top: temperatures for the desorption of a Pd monolayer from Ta(110), Mo(110), W(110), Re(0001), Ru(0001), and Rh(111). Bottom: Shifts in the Pd $3d_{5/2}$ binding energy of a Pd monolayer supported on several metal substrates. The shifts are reported with respect to the Pd $3d_{5/2}$ peak position for the surface atoms of Pd(100). Reprinted from ref. [32].

The type of correlation seen in Figure 9 has also been observed for Ni [22], Cu [22], Au [68] and Zn [69] overlayers. This suggests that in general the core level shifts do reflect changes in initial state induced by bimetallic bonding. And in most cases the formation of a strong metal-metal bond is associated with substantial perturbations in the electronic properties of the bonded metals [22, 23, 68, 69].

4. CO chemisorption studies

The electronic perturbations described in section 2 could affect the chemical properties of Pd. Carbon monoxide is an ideal molecule to investigate the chemisorption properties of bimetallic surfaces. There is extensive information about the surface chemistry of this molecule on many monometallic substrates [70], and the bonding mechanism is much better known for CO [14, 71, 72] than for other simple molecule. In addition, CO is involved in many catalytic processes of industrial importance [1, 4, 70].

Figure 10 displays CO-thermal desorption spectra acquired after adsorbing

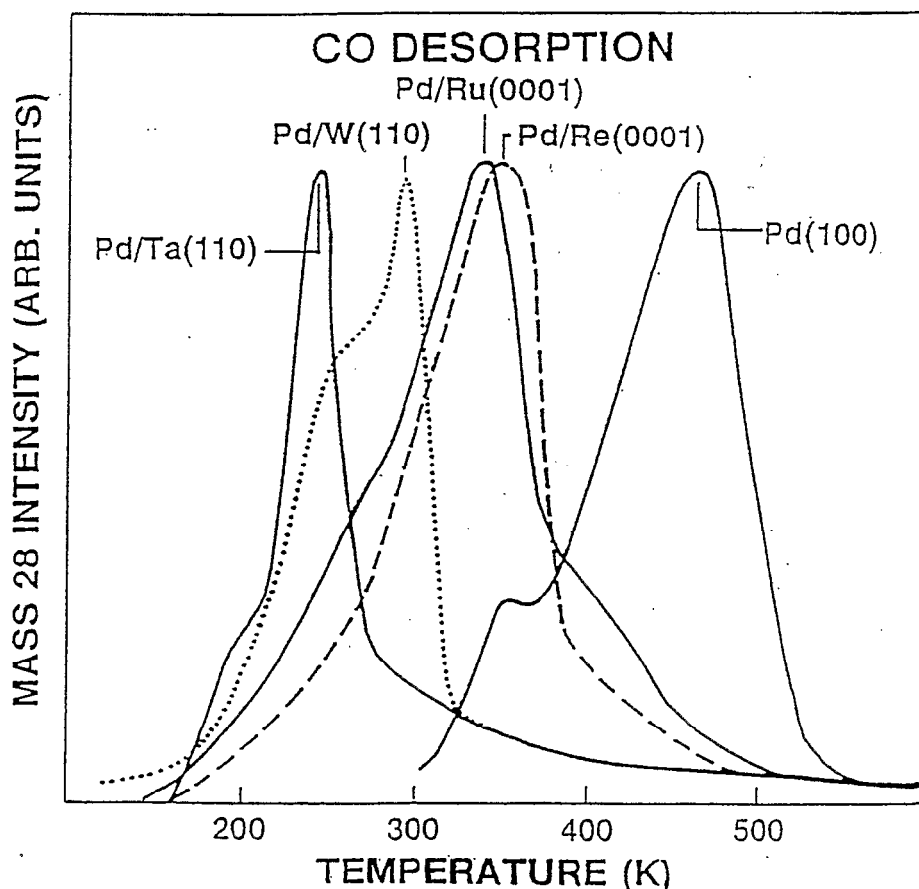


Fig. 10 CO thermal desorption spectra for Pd(100), and a monolayer of Pd supported on Re(0001), Ru(0001), W(110) and Ta(110). Reprinted from ref. [27].

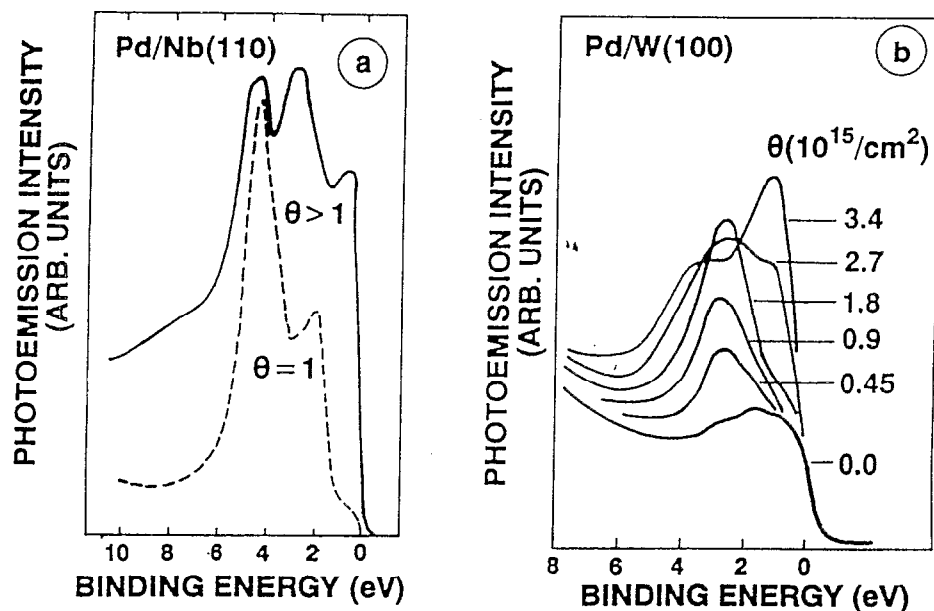


Fig. 1 (a) Ultraviolet photoelectron spectra for monolayer (dashed curve) and greater than monolayer coverages of Pd on Nb(110). (b) UPS spectra of various coverages (θ) of Pd on W(100). Reprinted from ref. [44].

Figure 2 displays photoemission spectra for the valence region of Pd/Rh(111) as a function of admetal coverage [32]. The $\text{Pd}_{0.9}/\text{Rh}(111)$ system exhibits a band structure that is very similar to that of Rh(111) or Pd multilayers. Difference spectra showed only minor electronic perturbations for supported Pd near the Fermi level [32].

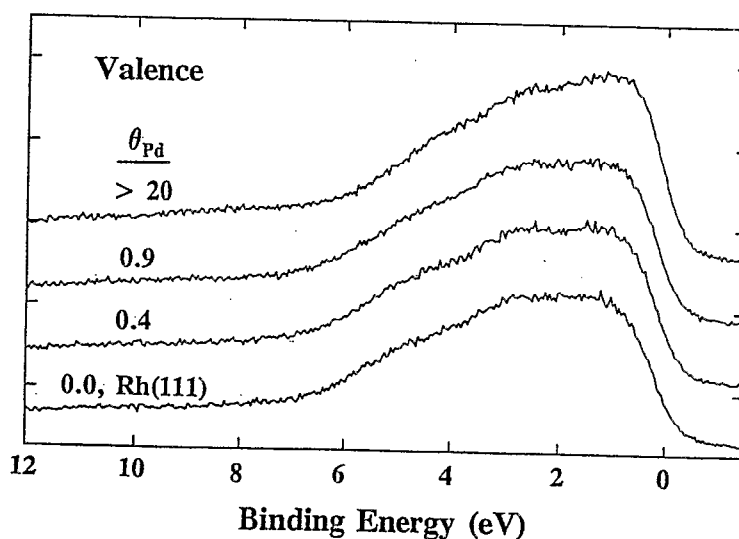


Fig. 2 Valence spectra for the bonding of Pd to Rh(111). Reprinted from ref. [32].

made feasible to study in detail electronic and chemical properties of bimetallic surfaces. Thus, many phenomena responsible for the behaviour of bimetallic surfaces have been identified [14-16]. Yet, several important issues associated with heteronuclear metal-metal bonding remain mysterious or badly understood [15,17,18].

In this chapter, an overview is presented of studies that deal with the electronic and chemical properties of Pd in bimetallic systems. We will focus on palladium for three main reasons. First, bimetallic catalysts that contain Pd or other Group-10 metals have many uses: isomerization of hydrocarbons, olefin hydrogenation, CO oxidation, alcohol synthesis, acetylene trimerization, etc. [8,10,19-21]. Second, palladium is very sensitive to the formation of bimetallic bonds [22-24]. And third, there is a vast number of experimental and theoretical articles in the literature that examine the properties of Pd in bimetallic systems [14,15,19-23,25-44]. From this large volume of work, one can get a general idea of how deep is our knowledge about the basic nature of bimetallic bonding and how it affects the properties of a metal.

The chapter is organized as follows. It starts with a description of photoemission and thermal desorption experiments for Pd overlayers on different types of metal substrates. General trends in the experimental data are examined and bonding models that explain them are discussed. Then, the validity of the bonding models is tested through *ab initio* or first-principles quantum mechanical calculations. From the combination of experiments and theory, a complete picture of the nature of bimetallic bonding is beginning to emerge.

2. PHOTOEMISSION STUDIES

Pd atoms bonded to surfaces of early-transition metals exhibit large electronic perturbations in their valence and core levels [15]. The valence photoemission spectra shown in Figure 1 for Pd/Nb(110) and Pd/W(100) illustrate this phenomenon [26,43,44]. In early studies examining the interaction of Pd with a Nb(100) surface [43], it was found that the supported Pd monolayer (ML) had a relatively narrow 4d band which exhibited a low density of states (DOS) around the Fermi level (E_F). In contrast, Pd multilayers and bulk palladium show emission spectra characterized by a large DOS at E_F . More recent photoemission studies for a Pd layer in contact with Ta(110) [25], W(100) [26], W(110) [26] and Mo(110) [15,45] also show a narrow Pd(4d) band with a centroid shifted toward higher binding energy. Thus, it appears that the bonding interactions between Pd and early-transition metals are quite strong. This will be confirmed below by results of thermal desorption mass spectroscopy.

the molecule on Pd(100), and on a Pd monolayer supported on Ta(110) [64], W(110) [67], Re(0001) [27] and Ru(0001) [27]. For CO on Pd(100) a desorption maximum is seen near 480 K, close to the temperature observed on Pd(111) and other flat Pd surfaces [27,67]. CO interacts strongly with pure Pd with an adsorption energy of ~ 35 kcal/mol [28,29]. For the Pd/Ta(110) and Pd/W(110) systems, the large decrease in the CO desorption temperature (180-230 K) indicates that there is a big weakening in the strength of the Pd-CO bond. The isosteric heat of adsorption of CO on the supported Pd monolayers is 15-20 kcal/mol smaller than on Pd(111) [28,29].

The valence photoemission spectra in Figure 11 were acquired after dosing

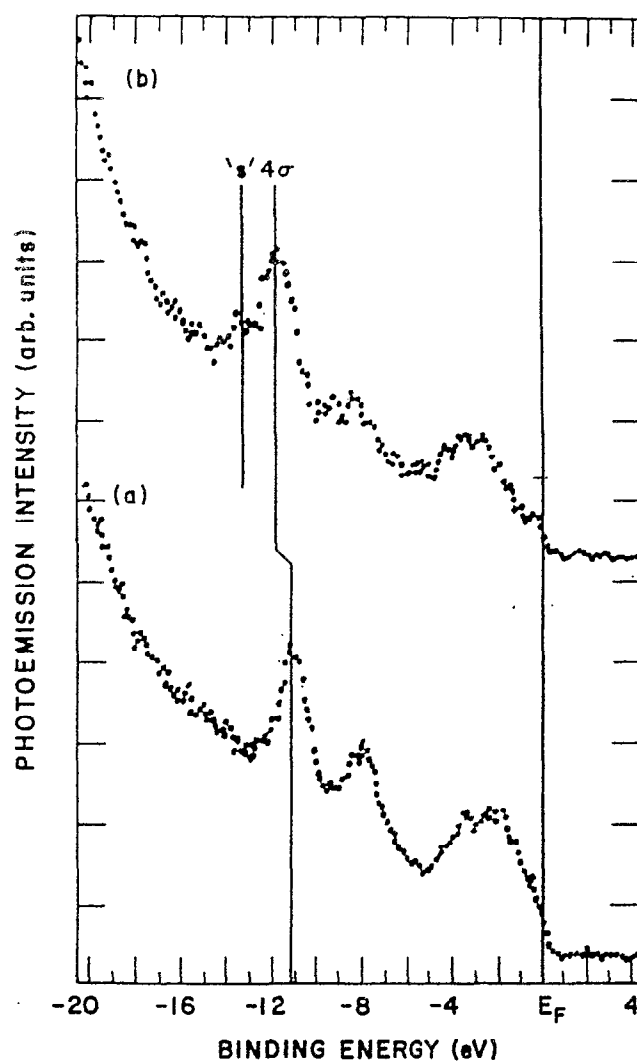


Fig. 11 Valence photoemission spectra for the adsorption of CO on Ta(110)-supported Pd films: (a) On a thick (> 3ML) Pd(111)-like film, (b) on a pseudomorphic Pd monolayer. Reprinted from ref. [30].

CO to a Pd(111)-like thick film and a Pd monolayer supported on Ta(110) [30,31]. The spectrum for a thick palladium film is in very good agreement with that observed for adsorption of CO on a single-crystal Pd(111) surface. The features at ~ 11 and 8 eV correspond to emissions from the 4σ and $(1\pi + 5\sigma)$ levels of CO, respectively [30,31]. In the photoemission spectrum for the Pd monolayer the 4σ and $(1\pi + 5\sigma)$ peaks of CO appear at higher binding energy than in the spectrum for the Pd(111)-like film, and there is also an extra “shake-up” satellite (‘s’ peak) around 13.6 eV. The spectrum for CO on the Pd monolayer matches the spectrum seen for CO on Cu(111) [30,31], where the bonding interactions between the ad molecule and metal substrate are much weaker than on Pd(111).

Evidence for weak bonding between CO and supported Pd monolayers is also seen in XPS experiments (see Figure 12) [27]. The adsorption of CO on Pd(100) produces a binding energy shift of ~ 1.2 eV in the 3d core levels of the metal surface (see Figure 13) [32,54]. On the other hand, a Pd 3d shift of only 0.6 eV is observed in Figure 12 for CO on Pd/Re(0001) [27]. In fact, Pd monolayers supported on Ta(110), Ru(0001) and Rh(111) also exhibit Pd 3d shifts upon CO adsorption smaller than that seen for the surface atoms of Pd(100) [32], as Figure 13 shows. There is a clear link between the strength of the Pd-CO bond and the CO-induced shift in the Pd 3d core levels of the

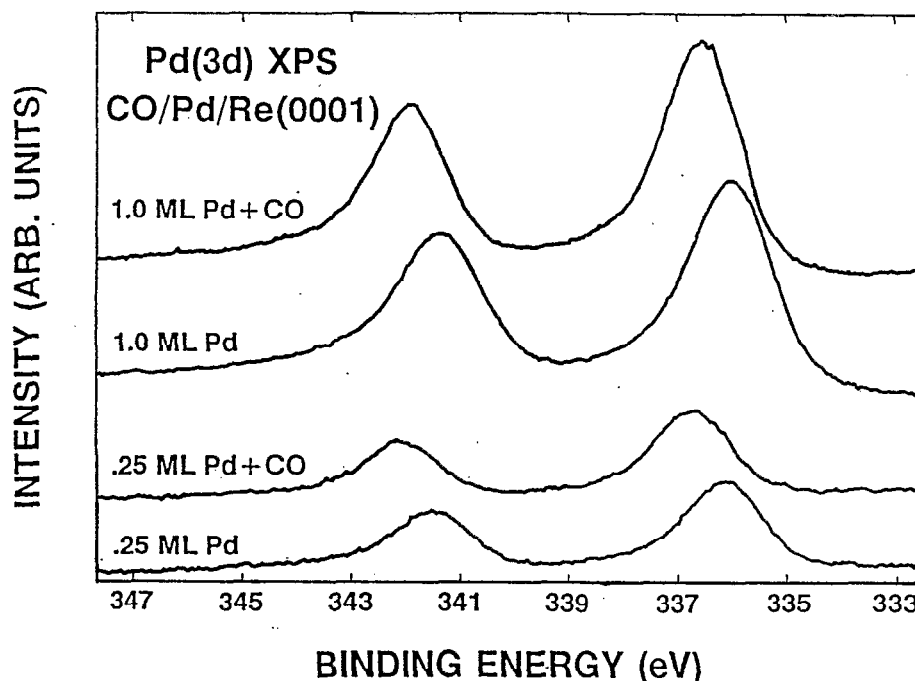


Fig. 12 Pd(3d) XPS spectra for clean and CO-saturated Pd on Re(0001). The Pd was deposited at ~ 350 K and annealed to 500 K before dosing 10 L of CO at ~ 115 K. Reprinted from ref. [27].

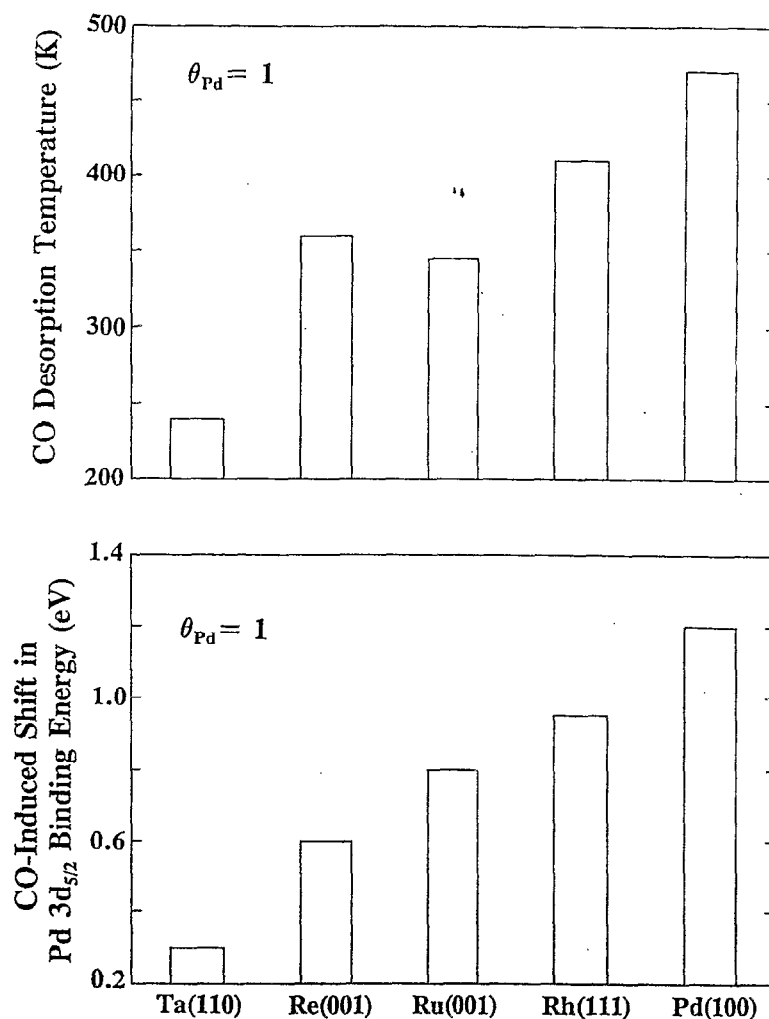


Fig. 13 CO desorption temperature and CO-induced shift on the Pd 3d_{5/2} binding energy for Pd(100) and Pd monolayers deposited on Ta(110), Re(0001), Ru(0001) and Rh(111). Reprinted from ref. [32].

bimetallic systems. Pd bonded to Ta(110) is not able to respond in an efficient way to the presence of CO, and essentially behaves as a noble metal. Infrared spectra for the CO/Pd/Ta(110) system show that CO is adsorbed linearly on top of the Pd atoms [28]. This is in contrast with the results typically seen for CO adsorbed on single-crystal Pd surfaces where hollow or bridging CO are the norm, but similar to that found for CO on many copper surfaces [28].

From the experiments described above it is obvious that bimetallic bonding can have a tremendous impact on the chemical properties of a metal. It is important to establish in what kind of bimetallic systems one can expect the largest changes in chemical behaviour. Figure 14 displays the desorption temperature observed for Pd-bonded CO on a series of bimetallic surfaces and

Pd(100) [15,27,35,64,67,73-77], together with the shift in Pd $3d_{5/2}$ binding energy found for each system before the adsorption of CO (i.e. *pure* metal-metal interactions, Figure 6) [15,25,27,35,46,53]. A clear correlation is seen between the changes in the electronic and chemical properties of Pd. The larger the shift in the Pd $3d_{5/2}$ binding energy induced by bimetallic bonding, the lower the CO desorption temperature from Pd. An identical trend is found when using the shifts in the Pd 4d valence band (shown in Figure 3) instead of the shifts in the Pd core levels. *The biggest chemical perturbations are observed for Pd atoms bonded to early-transition metals or s,p metals, in bimetallic systems that essentially involve the combination of an element with an electron-rich valence band (Pd) and an element with an electron-poor valence band.*

In general, for adlayers of the Group-10 metals, one finds positive binding-energy shifts in the core levels and a decrease in the CO desorption temperature (Figure 15) [22,23]. In contrast, Cu atoms deposited on late-transition metals exhibit negative core-level shifts and an increase in the desorption temperature

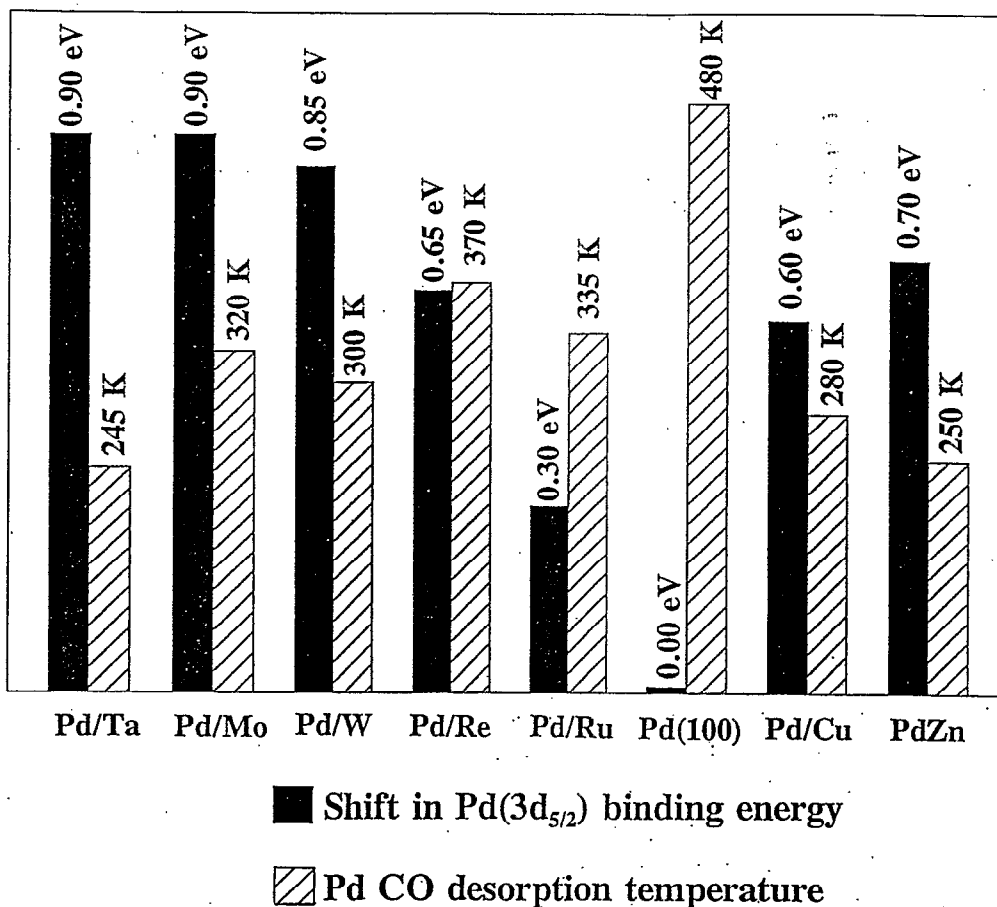


Fig. 14 Effects of bimetallic bonding on the properties of Pd. The graph displays the CO desorption temperature and the shifts in the Pd $3d_{5/2}$ binding energy with respect to the surface atoms of Pd(100). Solid bars: shift in Pd $3d_{5/2}$ binding energy; hatched bars: Pd CO desorption temperature. Reprinted from ref. [35].

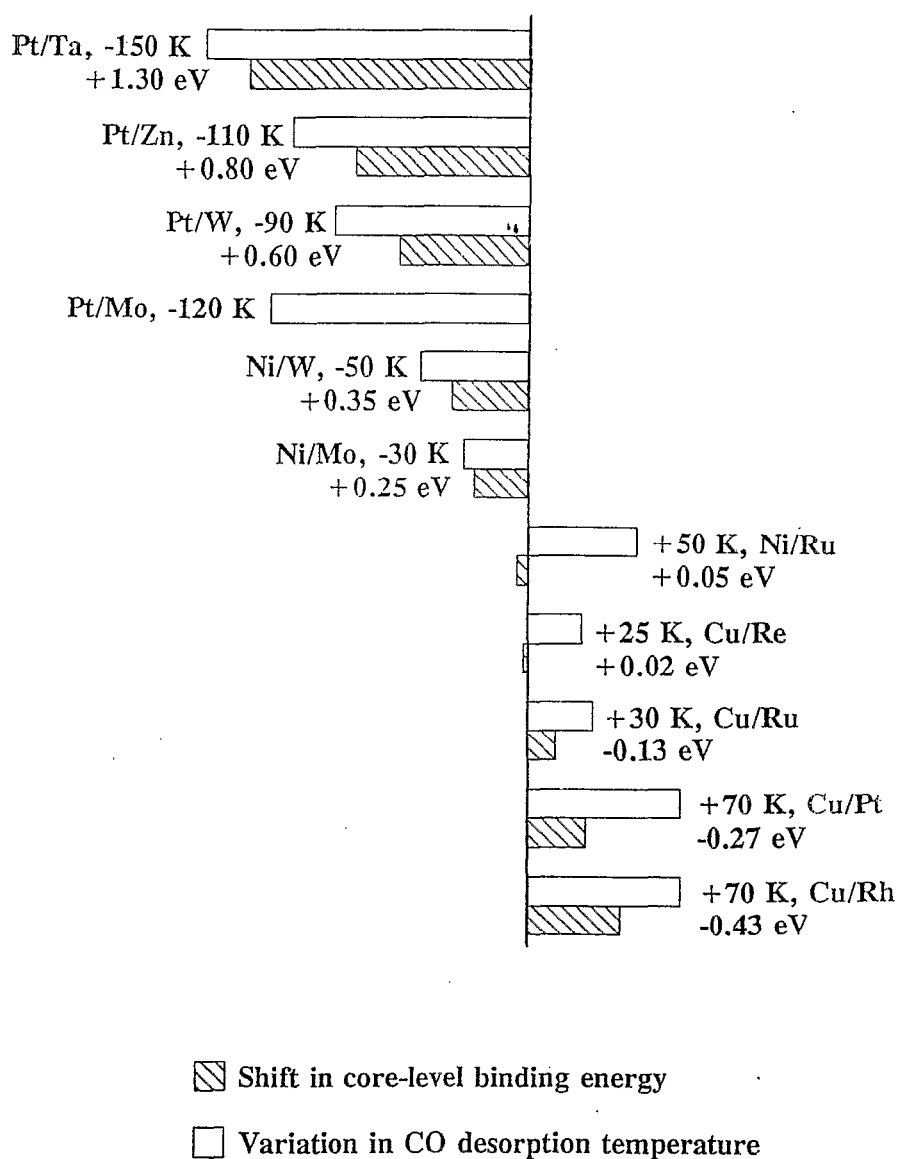


Fig. 15 Correlation between shifts in surface core-level binding energy (crossed bars) and the shifts in CO desorption temperature (empty bars). The properties of the Pt, Ni and Cu monolayers are compared with the corresponding values of the pure metals. Reprinted from ref. [15].

of CO (Figure 15) [22,65,78,79]. The electronic perturbations induced by bimetallic bonding deactivate Group-10 metals toward CO chemisorption, whereas the same type of phenomena activate Cu [65,78,79] and Au [80] adatoms.

Bimetallic bonding can also produce interesting changes in the reactivity of a metal towards hydrogen [15,43,81-83]. Experimental evidence indicates that

hydrogen dissociatively chemisorbs on Pd/Nb(110) at ~ 300 K when $\theta_{\text{Pd}} > 1$ ML, but no (or little) hydrogen adsorbs when $\theta_{\text{Pd}} = 1$ ML [43,81]. A similar behaviour is seen for the interaction of H_2 with Pd/Ta(110) [82] and Pd/Mo(100) [83]. Electronic perturbations reduce the adsorption energy of ethylene on a Pd monolayer supported on Mo(100) [84]. Ethylene is weakly chemisorbed on the Pd monolayer (desorption temperature ~ 250 K against ~ 290 K on pure Pd), and the adsorbed species is much less rehybridized from sp^2 in the gas phase toward sp^3 on this surface compared to C_2H_4 chemisorbed on the (100) face of pure Pd [84].

5. MODELS FOR BIMETALLIC BONDING

The experimental results in Figures 9, 13, 14 and 15 show strong correlations between the electronic and chemical properties of an element in a bimetallic surface. In the early 1990s, it became clear that the electronic perturbations induced by bimetallic bonding are associated with the strength of the heteronuclear metal-metal bond [27], and that these perturbations can determine the chemical reactivity of a bimetallic surface [22,44]. To explain the correlations in Figures 9, 13, 14 and 15 a model for bimetallic bonding was proposed [22,27,44]. There were three basic assumptions in the model. First, on the basis of the correlations in Figures 9 and 14, it was assumed that the shifts in the core levels reflected real changes in the initial state of the Pd electrons. Second, since the largest electronic perturbations were found in systems that involved "electron-rich + electron-poor" metal combinations (i.e. Pd/Ta, Pd/W, etc) with an admetal-induced reduction in the work function of the metal substrate, it was thought that bimetallic bonding produced some transfer of electrons ($\text{Pd}^{\delta+}$) which eventually led to positive shifts in the core and valence levels of palladium. And third, it was proposed that the electronic perturbations in Pd reduced the strength of the Pd-CO bond by weakening π back-bonding. On metal surfaces the CO chemisorption bond is dominated by interactions between the occupied valence levels of the metal and the LUMO (2π orbital) of the adsorbate (π back-bonding) [71,72]. For supported Pd the 4d valence band is more stable than in pure Pd, probably weakening π back-bonding and leading to smaller CO adsorption energies [44,85]. At the time, this model for metal-metal bonding offered a logical and consistent explanation for the experimental facts [22,27,44]. Its three basic assumptions had to be validated by additional experimental and/or theoretical work.

Photoemission studies have shown that in many cases the formation of a bimetallic bond induces positive core-level shifts for *both* metals [17,86,87,88,]. This, obviously, is not consistent with a simple metal-metal charge transfer [60,90]. The phenomenon could be a consequence of combining inter- and intra-atomic charge redistributions (for example, d-sp rehybridization) induced by

bimetallic bonding [23,51,60,90]. Thus, the bond between two different metals can be quite complex [17]. Theoretical studies have been useful for clarifying this issue and other aspects associated with heteronuclear metal-metal bonding.

6. THEORETICAL STUDIES

6.1 Charge redistribution in bimetallic bonding

The nature of the bond between Pd and surfaces of transition or s,p metals has been the subject of a large series of theoretical works [23,33,34,35-42,89-91]. From these studies, it is clear that the Pd-substrate bond is best described as metallic with a small degree of ionic character. The direction of the net charge transfer (i.e. Pd→substrate or substrate→Pd) varies from one calculation to the other. This discrepancy can be attributed to the lack of charge self-consistency in some of the calculations, and to the intrinsic difficulties associated with determining charge transfer, especially when the net amount of electron density transferred is small. The different schemes used for partitioning the electron population of each atom are more or less arbitrary [90,92,93], and in practice, the results of a given type of analysis can only be justified by comparing against the trends or predictions of experimental measurements. A reasonable approach is to plot the electron density around a metal atom and observe any possible change in the spatial distribution of the electrons [33,34,40,94].

The calculated electron density for a Pd monolayer supported on Ta(110) is plotted in Figure 16. These results are from first-principles density-functional calculations with the full-potential linearized augmented plane-wave (FPLAPW) method [33,34]. A strong Pd-Ta bonding interaction can be seen in the charge density difference shown in Figure 16c, where electrons deplete from both the interfacial Ta and Pd sites and accumulate in the region between them [33,34]. The more significant charge redistribution occurs around the Pd atoms, with the average center of electrons shifting away from the plane of Pd nuclei toward the substrate. The complex nature of the bimetallic bond in the Pd/Ta(110) system leads to positive core-level shifts for Pd and Ta [27,33,90,95,96]. The Pd-Ta bond cannot be classified as a simple "metallic" or "ionic" bond [33,34]. It involves an important shift of electrons from the Pd atom toward the Ta substrate, as the work function and Pd core levels suggest [48,97], and a simultaneous electron depletion around Ta, as the Ta core-level shifts and a simple Pd-Ta "covalent" interaction imply [87,90,96,97].

The FPLAPW method has also been used to study bimetallic bonding in Pd/W(110), Pd/Re(0001) and Pd/Ru(0001) [34]. In general, electron density plots show an important shift of electrons from the Pd layer toward the metal-metal interface. A similar result has been found in first-principles density-functional slab calculations for Pd/Mo(110) [40,98]. The larger the movement of

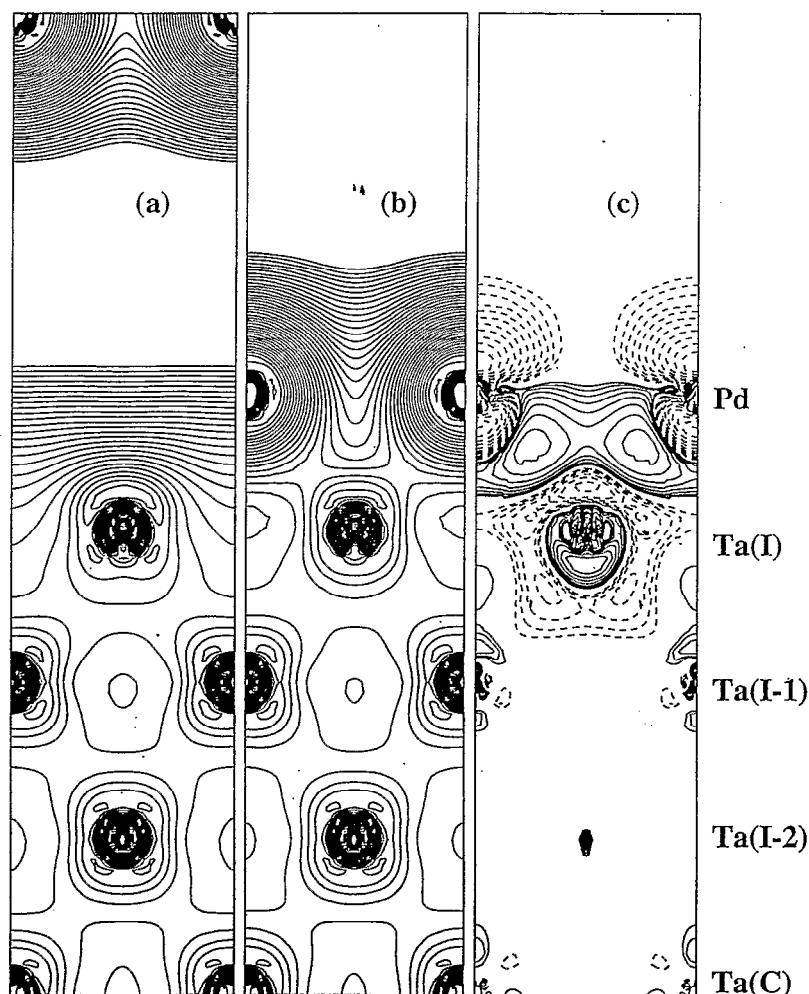


Fig. 16 (a) Calculated valence charge density for a Pd monolayer (top) and clean Ta(110). (b) Calculated valence charge density for the Pd/Ta(110) system. (c) Charge density difference obtained by subtracting the superposition of the charge densities of the Pd monolayer and Ta(110) from that of Pd/Ta(110). Dashed lines indicate a decrease in the electron density. Reprinted from ref. [33].

electrons from around Pd to the metal-metal interface, the stronger the bimetallic bond [34,98]. The charge redistribution around Pd is in part caused by a Pd(4d)-Pd(5s,5p) rehybridization that accumulates electrons in the bimetallic bonds [23,98]. Such a rehybridization has been observed in many theoretical studies, using different levels of theory and cluster or slab models [23,37-39,41,48,98]. In general, this redistribution of electrons is more significant than the net charge transfer between the Pd overlayers and metal substrates.

From studies of x-ray absorption spectroscopy [51,52], it is known that Pd has a tendency to lose d electrons when forming bulk intermetallic compounds.

Figure 17 shows the calculated 4d electron population for a Pd atom bonded to clusters that model hollow sites of Al(111), W(110), Rh(111) and Pd(111) [23,32]. After comparing the results for Pd/Rh₉ and Pd/Pd₉, one can conclude that Rh induces minor changes in the electron distribution around the Pd atoms. This is consistent with the photoemission results in Figures 2 and Figure 9. For a Pd/Rh system the loss in the Pd 4d population, as a consequence of a d-s,p rehybridization and a Pd-substrate shift of electrons, is smaller than for Pd/Al and Pd/W systems [32]. The qualitative trends in Figures 3, 6 and 17 are identical: as the fraction of empty states in the valence band of the substrate rises, there is an increase in the magnitude of the electronic perturbations in Pd. A similar correlation is observed in DF slab calculations for the bimetallic systems [34,98].

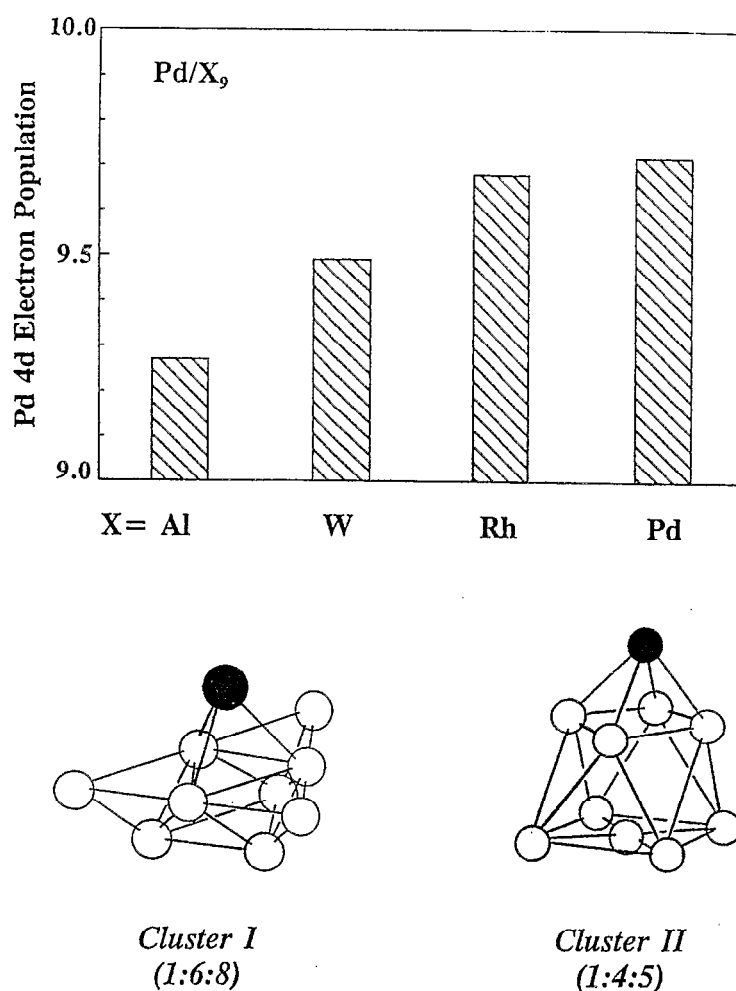


Fig. 17 Bottom: Pd/X₉ clusters used to study the adsorption of a Pd atom (dark sphere) on several metal surfaces. Cluster I models the bonding of Pd to an fcc hollow site of Al(111), Rh(111) or Pd(111). Cluster II models the adsorption of Pd on a hollow site of W(110). Top: calculated 4d electron population for the Pd adatom in the Pd/X₉ clusters. Reprinted from ref. [32].

6.2 Core-level and valence-band shifts

The redistribution of charge and d-s,p rehybridisation observed in many theoretical calculations [23,33,34,37-39,40,41,48,98] should affect the position of the core levels and valence band of palladium. The Pd(4d) orbitals are more compact than the Pd(5s,5p) orbitals and, therefore, exhibit larger Coulomb interactions with the core electrons of palladium [23,60,99,100]. Thus, a d-s,p rehybridisation reduces electron-electron repulsion and should shift the Pd core levels and 4d band toward higher binding energy [51,60].

Early theoretical studies based on a semi-empirical self-consistent tight-binding scheme indicate that the core-level shifts in the Pd/W(110) and Pt/W(110) systems come from initial state effects (d-s,p rehybridisation, for example) [37]. The calculated shift for the Pd 3d_{5/2} core level was 0.7 eV versus the value of 0.8 eV measured experimentally [53]. More sophisticated calculations (full-potential linear muffin-tin orbital method with LDF) for the Pd/Mo(110) system also indicate that the Pd 3d core-level shifts reflect initial state effects (substantial polarization of electrons around Pd) [40]. In this case, the calculated Pd 3d_{5/2} core level (0.9 eV) is identical to the experimental value and most of it (0.77 eV) comes from initial state effects while the rest (0.13 eV) originates in changes in the screening of the core hole [40].

Figure 18 summarizes results of calculations with the FLAPW method for Pd/Ta(110), Pd/W(110), Pd/Re(0001) and Pd/Ru(0001) [34]. At the bottom of the figure are shown the calculated and experimental Pd 3d_{5/2} core level shifts as a function of the calculated bonding energy for Pd (E_b) on each substrate. For the Pd/Re and Pd/W systems, the agreement between theory and experiment is very good. Discrepancies can be seen for the Pd/Ru and Pd/Ta systems. In general, the theoretical results imply that the core-level shifts measured experimentally mainly derive from initial state effects [34,90]. A strong correlation is obvious between the core-level shifts (for both the calculated and the measured results) and the bonding energy. For the calculated results, there is linearity for Pd/W, Pd/Re, and Pd/Ru, but not for Pd/Ta(110). Experimentally, by contrast, good linearity develops for Pd/Ta, Pd/W and Pd/Re but not for Pd/Ru(0001). The reasons for this discrepancy are not clear [34].

Theoretical studies show that bimetallic bonding increases the stability of the Pd 4d valence band [14,23,34,36,40,90,98]. The variation in surface core level shifts for metal overlayers is accompanied by a similar shift in the center of gravity of the admetal d band [34,40,90]. In the top panel of Figure 18 is shown the calculated density-of-states (DOS) at the Fermi level for a palladium monolayer on four different metal substrates. As one moves from Pd/Ru to Pd/Ta, there is a substantial drop in the DOS at E_F (i.e. the noble metal character of the bimetallic system increases). This agrees with the experimental results seen in Figure 1. Interestingly, a direct (almost linear) relationship between the

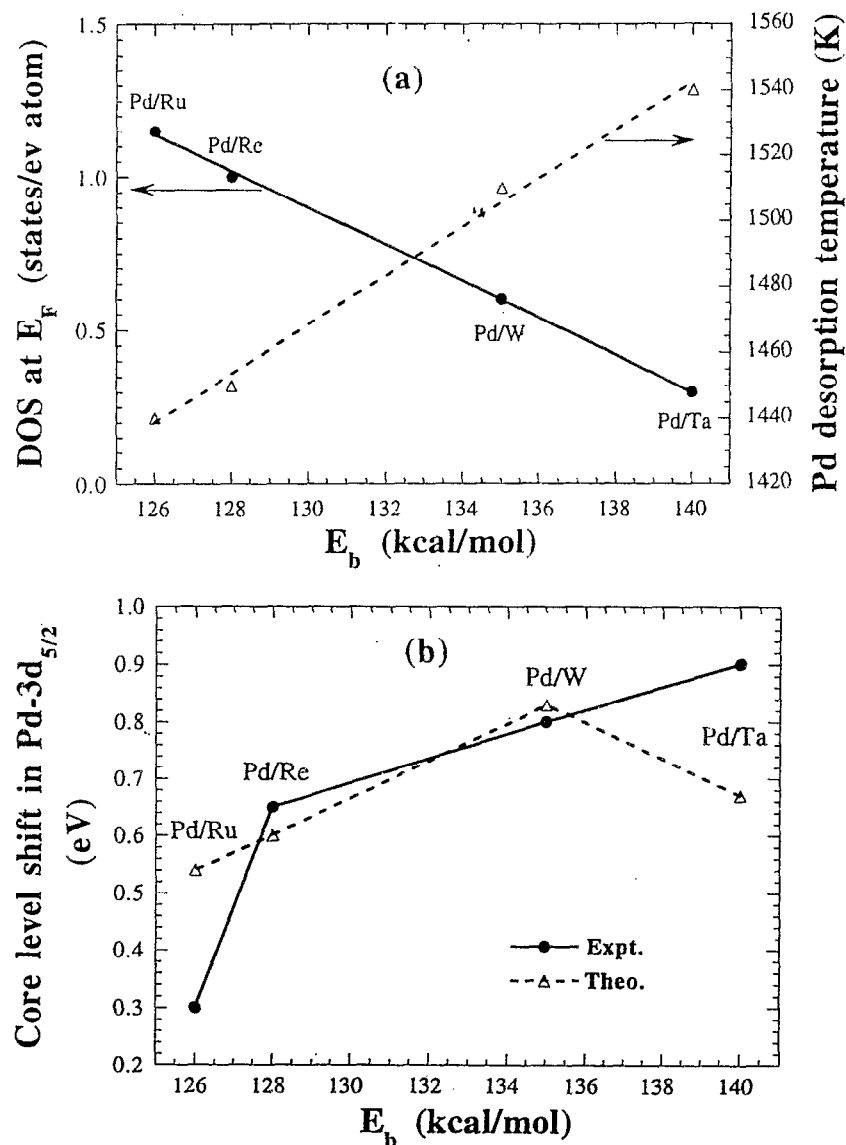


Fig. 18 Interaction of a Pd monolayer with Ru(0001), Re(0001), W(110) and Ta(110). Part (a): Calculated value for the density-of-states at the Fermi level and the measured desorption temperature as a function of the theoretical bonding energy. Part (b): Experimental and theoretical palladium 3d_{5/2} core level shifts versus the calculated bonding energy. Reprinted from ref. [34].

bonding energy and the value of the DOS at E_F for Pd atoms is observed in Figure 18. Such behaviour can be understood since a substantial redistribution of charge results in both a larger energy shift for the valence states and a larger bonding energy [34].

DF slab calculations have been used to study in a systematic way the effects of bimetallic bonding on the valence band of Pd and many other metals [14,36,101,102]. For metal overlayers, the strain induced by the metal substrate

on the structural configuration of the overlayer has a direct influence on the position and width of the admetal valence band [14,102]. The supported Pd monolayers in the bimetallic systems of Figure 18 all adopt a pseudomorphic structure with respect to the metal substrates [27,53,66,67]. In the cases of Pd/W(110) and Pd/Ta(110), this pseudomorphic configuration leads to a substantial stretching of the Pd-Pd distances with respect to those seen in bulk Pd or the Pd(111) and Pd(100) surfaces [27,53]. The weaker the Pd-Pd interactions, the stronger the Pd-substrate interactions and the electronic perturbations on Pd. The case of Pd/Re(0001) is particularly interesting, since in this system the metal overlayer has an atomic density that is not very different from that of Pd(111) [27], and the pure effects of metal-metal bonding shift the Pd 3d core levels and 4d band.

6.3 CO chemisorption

The bonding mechanism between CO and a metal involves electron transfer from the CO(5σ) orbital into the empty bands of the metal, σ -donation, and electron transfer from the occupied bands of the metal into the CO(2π) orbitals, π -backdonation [36,71,72]. From a thermochemical viewpoint, π -backdonation is energetically more important than σ -donation [71,72]. In principle, a positive shift in the Pd 4d band (Figures 3 and 18) and a decrease in the Pd 4d population (Figures 16 and 17) should reduce the ability of this metal to donate electrons into the CO(2π) orbital and weaken the Pd-CO bond. The experimental results in Figure 13 are in complete agreement with this idea. When Pd is deposited on metal substrates like Ta or Re, there is a reduction in the CO desorption temperature (weaker Pd-CO bonding) and in the magnitude of the shift induced by CO on the Pd 3d levels (decrease of π -backdonation [27,32]).

Several theoretical studies have shown a relationship between a reduction in π -backbonding and the weakening of the Pd-CO on palladium overlayers: CO/Pd/Ti(001) [42,98], CO/Pd/W(110) [41,98,103], CO/Pd/Mo(110) [40,98], CO/Pd/Ru(0001) [36,42], CO/Pd/Rh(111) [98], CO/Pd/Cu(111) [104], and CO/PdCu [38]. In some surfaces of bulk alloys, PdCu(111) and Pd₃Mn(100), DF calculations show a weakening of the Pd-CO bond without a decrease in π -backdonation [91,105]. In addition to a reduction in π -backdonation, a weakening of the Pd-CO bond may result from a decrease in 5σ donation, variations in Pauli repulsion between adsorbate and surface, and changes in electron correlation [36,91,98,105].

Trends for the adsorption of CO on many bimetallic systems can be reproduced by a simple tight-binding model that includes the interactions between the metal d states and the CO 2π and 5σ states, renormalized by the metal s,p continuum [36]. Figure 19 shows the scaling of the chemisorption energy for CO within the model as compared to results of DF slab calculations

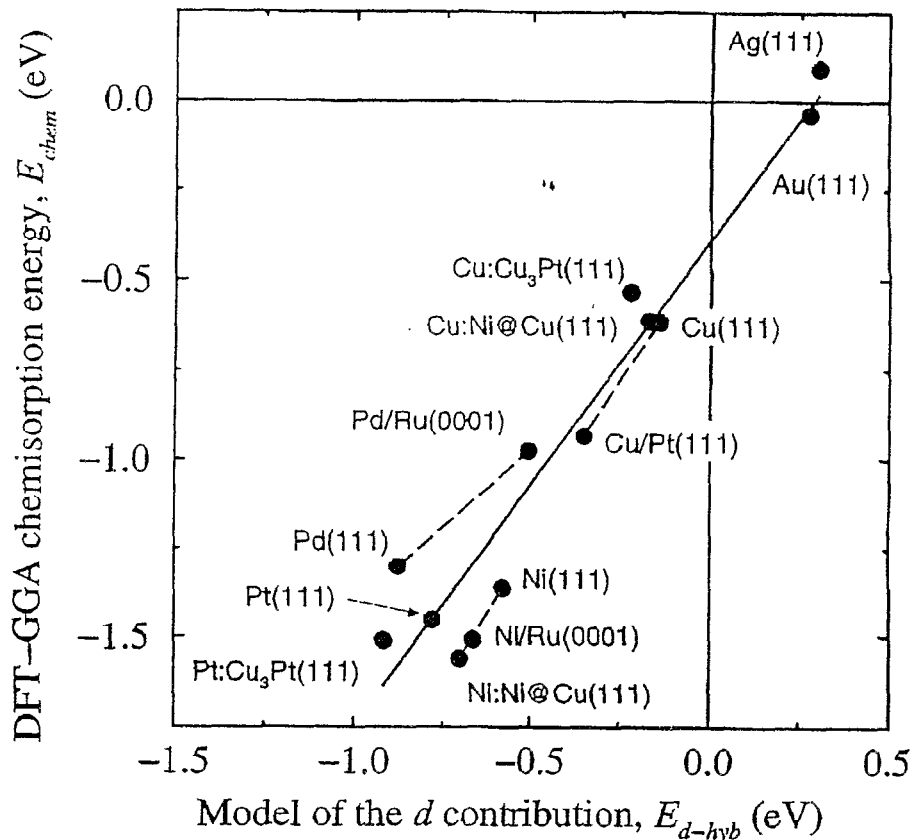


Fig. 19 Comparison of CO chemisorption energies calculated with a tight-binding model and full DF-GGA calculations. Reprinted from ref. [36].

[36]. The good agreement indicates that the interactions included in the tight-binding model are responsible for the gross trends in CO chemisorption energies for the monometallic and bimetallic systems examined. The dominant contribution to the E_{d-hyb} term comes from the hybridisation or mixing of the metal d band and CO 2π orbitals [36]. The energy released by this hybridisation decreases when going from CO/Pd(111) to CO/Pd/Ru(0001) [36] or CO/Pd/Cu(111) [104].

The electronic perturbations which reduce the ability of palladium to π -backdonate electrons to CO also limit electron transfer into the LUMO's of H_2 , C_2H_4 and SO_2 [98,106]. For these adsorbates, theoretical calculations predict small adsorption energies and no dissociation if palladium is supported on early-transition metals [98,106].

7. CONCLUSION

The experimental and theoretical studies described above illustrate the complex nature of the heteronuclear metal-metal bond. In many cases, bimetallic bonding induces a significant redistribution of charge around the bonded metals. This redistribution of charge is usually linked to the strength of the bimetallic bond, affects the position of the core and valence levels of the metals, and can determine the chemical reactivity of the system under study. New concepts are emerging [22,23,34,36] and eventually the coupling of experiment and theory can be useful for designing more efficient bimetallic catalysts [98,106,107].

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